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A case study in a Brazilian rain forest reserve

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SUMMARY

The *Parque Estadual Turístico do Alto Ribeira* (PETAR) is an Atlantic rain forest reserve in South-eastern Brazil. A few small villages are located inside the watersheds of the three main rivers that cross the park, Betari, Iporanga and Pilões. Untreated domestic sewage from households is often discharged directly into the watercourses. Subsistence agriculture is practiced by most of those families, which adds nutrients to the stream due to increased soil erosion. Additionally, larger farms located near the headwater of PETAR rivers use fertilizers to improve soil condition. The main goal of this study is to investigate seasonal and spatial variability in nutrient concentration in PETAR watercourses due to inputs from human settlements and agricultural areas within or near the park.

Twenty-one sites located in fifteen streams were surveyed during field campaigns carried on in June and November 1998. Nitrogen and phosphorus concentration, as well as other physical and chemical water parameters (temperature, pH, dissolved oxygen, conductivity, hardness and alkalinity), were measured.

Most of the seasonal and spatial chemical variability of the surveyed streams can be explained by natural factors such as bedrock characteristics, topography and climate conditions. However, anthropogenic factors may also affect the quality of PETAR streams. At the headwaters of Iporanga and Pilões Rivers an increase in nutrient concentration was observed. That can be a consequence of domestic sewage discharge, fertilizers application in agriculture or even use of explosives containing nitrogen in mining activities. Indication of early stages of eutrophication (observed increase in plant biomass and measured increase in nutrients availability and chemical demand of oxygen) was found in Monjolos Stream downstream outlets of domestic sewage from the village of Bairro da Serra.

Keywords: nutrient, eutrophication, rainforest, tropical watercourses

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Foreword

This report shows partial results of two field trips (June and November 1998) carried out in the *Parque Estadual Turístico do Alto Ribeira* (PETAR), state of São Paulo, Brazil. The study is part of Johanna Lundqvist's Master Thesis, student of the International Master Program "Applied Environmental Measurement Techniques", at Chalmers University of Technology. The study is also a component of a larger project, which is an Ecological Risk Assessment (ERA) of Human Impacts in PETAR, by Rosana Moraes and Sverker Molander from the Environmental Systems Analysis, also at Chalmers.

The geological aspects of this report have been discussed by PhD Helio Shimada, a researcher at the *Instituto Geológico* in São Paulo, Brazil, who previously coordinated an extensive geological study in PETAR area (Shimada, 1999) and participated in the first field trip described in this report.

The results presented here will be further discussed in Lundquist, (in preparation) and in future publications by the authors and their collaborators. The description of the ERA project, as well as a detailed characterization of physical, social and economical aspects of the study area can be found in Molander and Moraes (1998), and Moraes and Molander (1999).

Introduction

The *Parque Estadual Turístico do Alto Ribeira* (PETAR) is located in the Southwestern part of São Paulo State, in the Ribeira Valley. It is one of the most preserved areas of Atlantic rain forest in Brazil. However, the main rivers that cross PETAR and their tributaries flow through areas where different types of land use may influence ecosystems inside the park (Figure 3). These types of land use include agriculture, human settlements and mining (Moraes and Molander, 1999 and Shimada *et al.*, 1999a).

According to the Environmental Secretariat of São Paulo (Secretaria do Meio Ambiente do Estado de São Paulo, 1991), there are approximately fifteen small villages inside, or in the vicinity of the reserve. These villages are composed by small groups of families (Figure 1), most of them surviving on subsistence agriculture, poaching and gathering (Moraes and Molander, 1999). The largest village is Bairro da Serra (Figure 2). Its population has expanded during the last decades due to the increase of tourism in PETAR and the collapse of the mining activities in the region (Secretaria do Meio Ambiente do Estado de São Paulo, 1997a). Few hostels are found in the village, which are fully occupied by tourists during holiday seasons.

Figure 1: Village Pilões, located near Pilões River.

Photo: *R. Moraes*

Figure 2: Bairro da Serra Village, located near Betari River.

Photo: *H. Shimada*

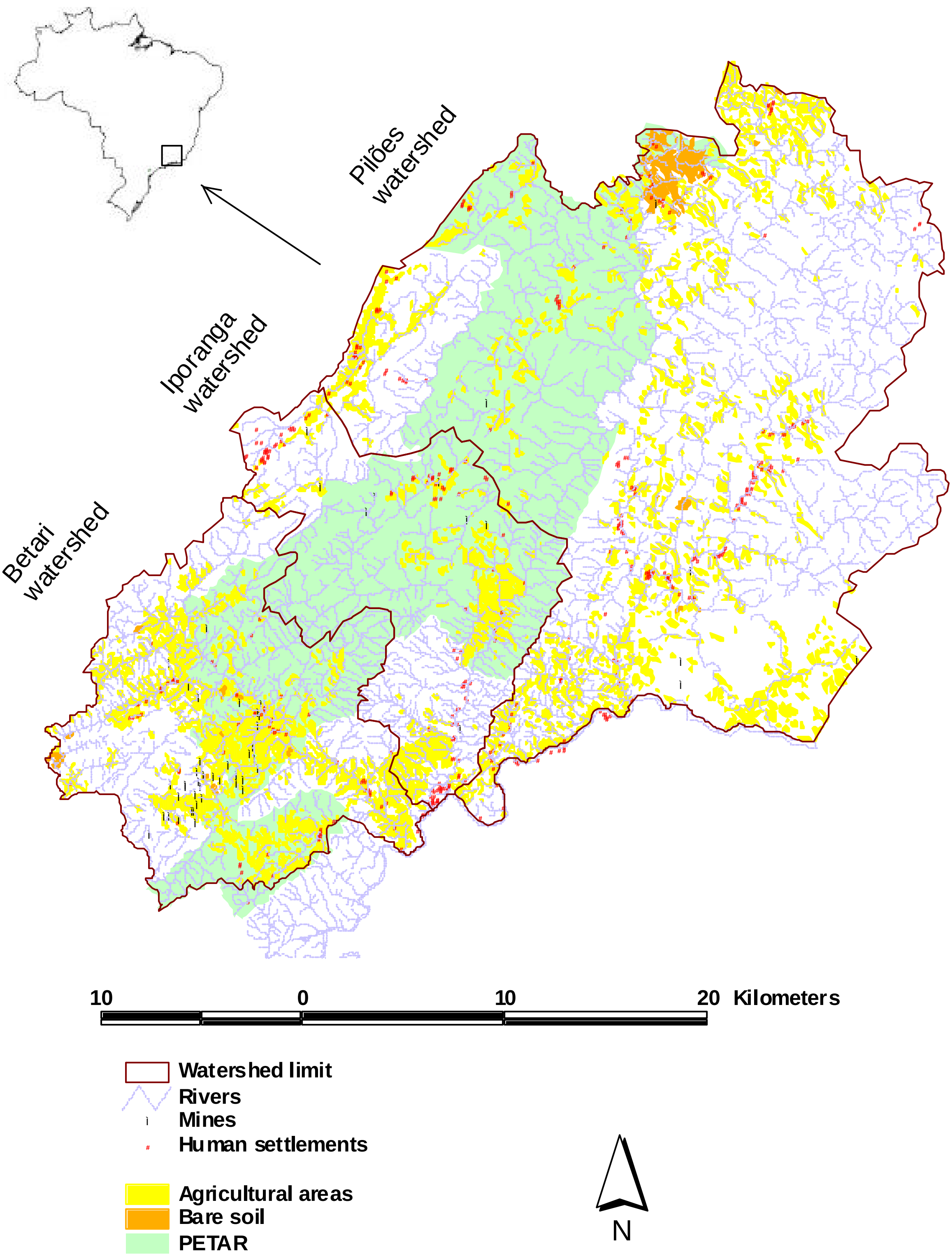


Figure 3: Schematic map of the study area showing sources of pollution, rivers, boundaries of Betari, Iporanga and Pilões watersheds and PETAR limits[a].

[a] Sources: (Secretaria do Meio Ambiente do Estado de São Paulo, 1986; Instituto Brasileiro de Geografia e Estatística, 1987; Secretaria do Meio Ambiente do Estado de São Paulo, 1997b; Shimada *et al*., 1999b)

Since most of the houses do not have a proper sewage treatment, domestic discharges are released directly into the watercourses (Moraes and Molander, 1999). Possible effects are related to the decrease of oxygen concentrations in water due to breakdown of organic compounds present in sewage. Further downstream to the outlets, the increase in nutrients may cause eutrophication, i.e., a change towards a more nutrient-rich condition in the watercourse. This may lead to an increase in algal and macrophytal biomass (Figure 4), if no other factor limits the process (Swedish Environmental Protection Agency, 1993).

There are also some small farms in the region (Figure 5) where farmers cultivate, among other crops, tomato, peaches, corn, beans and pumpkins, and rise livestock. Use of fertilizers and increase in erosion in agricultural fields may add nutrients to the watercourses by contamination of groundwater or run off from land. In both cases, the phosphorus and nitrogen leaking from the terrestrial environment may cause eutrophication (Swedish Environmental Protection Agency, 1993).

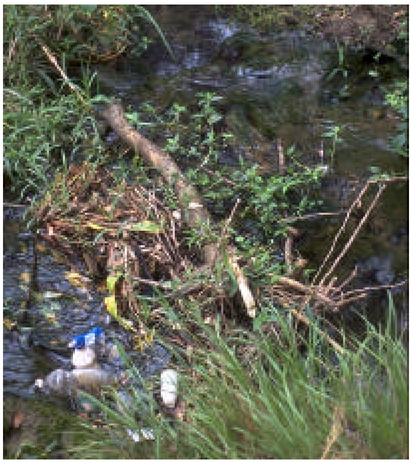


Figure 4: Solid waste accumulation and increasing of algal and macrophytal biomass in Monjolos streams, downstream Bairro da Serra.

Photo: J. Lundqvist.

Figure 5: Agricultural area in the vicinity of PETAR.

Photo: S. Molander

The objective of this study is to investigate the range of seasonal and spatial variability in nutrient concentration in PETAR watercourses due to inputs from human settlements and agricultural areas within or near the park. Since the nutrient availability for uptake by plants and bacteria is affected by physical and chemical water characteristics, several river water parameters were measured during the study.

Material and methods

General characterization of the study area

The altitude of the hilly terrain of the park varies from about 100 to 1000 m above the sea level. Most of its 35.712 hectares is situated on the Paranapiacaba Mountain Ridge. Together with the other neighbor reserves - Fazenda Intervales State Park, Serra do Mar Environmental Protection Area, Xitue Ecological Station and Carlos Botelho State Park - it constitutes one of the most protected areas of the state of São Paulo. Those five areas represent more than 400.000 hectares of protected Atlantic Rain Forest.

The climate is classified as mesotermic humid (Cfb), according to Köpper (Lepsh 1988). Two air masses affect the region during a year. The Atlantic Tropical air mass is the most prevalent, and influences the rain distribution. The influence of the Atlantic Polar air mass just lasts for a short period during the winter season. The dry period occurs between April to September.

Geology of PETAR region is mainly characterized by rocks of the Açungui Group. This group is a thick sequence (about 5.500 m according to Campanha and et al., 1985) of metasedimentary and metavolcanic rocks with ages ranging from the Middle to the Upper Proterozoic. The Açungui Group is represented by the stratigraphic units Perau Formation, Iporanga Formation, Lajeado Subgroup, Itaiacoca Formation, Córrego do Marques Formation and the Apiai Schists. The last tree units occur out of the limits of PETAR and their expositions can be found in the Apiaí (Apiai Schists) and Ribeirão Branco region (Itaiacoca and Córrego do Marques Formation). These rocks were deformed and metamorphosed by tectonic action in the Upper Proterozoic. Granitic bodies intruded the metasedimentary ensemble from the Upper Proterozoic to the Cambro-Ordovician. The Samambaia conglomerate in the NW of PETAR locally represents an Early Cambrian restricted sedimentary basin. Anticlines and synclines with NE-SW axis and NE-SW shear zones with tens of kilometers in length are the most prominent geological structures in the region. In the Mesozoic, a system of NW-SE diabase dikes have cut the older rocks. The Betari River is placed along one of these dikes. Quaternary unconsolidated sediments occur as irregular alluvial spots along the major rivers.

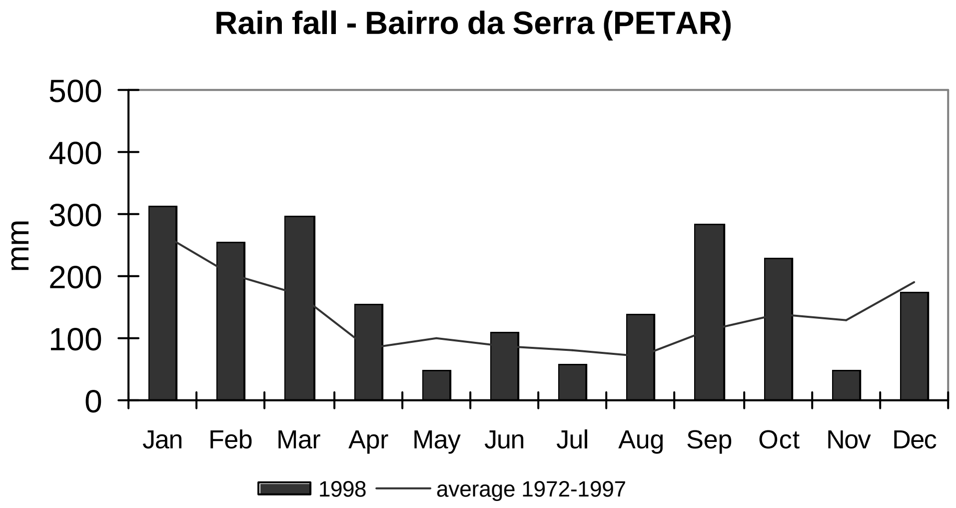
Older rocks belonging to the Lower Proterozoic Santana Metamorphic Suite, Apiaí-Mirim Complex and Setuva and Água Clara Formations occur out of the limits of PETAR to the W-NW and S-SE.

The main lithologies of the Açungui Group in PETAR and in its close neighbourhood are metacarbonatic rocks (metalimestones, metadolomites and marbles), metapelites, metasiltites, metasandstones and quartzites. Metabasites and acidic metavolcanic rocks are found in the eastern limit of PETAR associated to the metasedimentary rocks of the Perau Formation, which also present iron formations. The mineral associations of the lithological units indicate a low-grade metamorphism, in the zone of chlorite. Granites of Espírito Santo and Vargem Grande Mass are found in the western sector of PETAR and their contact zones with the metasediments show contact metamorphism aureoles.

Sampling campaigns

Field trips took place during the dry-cold (07 - 17.06.98) and rainy-warm season (13 - 22.11.98). The purpose was to compare possible seasonal differences in physical and chemical water parameters.

The average monthly temperature varies between 14^{o}C in July at high altitudes and 25 ^{o}C in January at low altitudes (Figure 6). Average precipitation varies between 90 mm (winter) and 280 (summer). The year 1998 was quite unusual in terms of precipitation. November normally correspond to the beginning of the rainy season (average rainfall in November as 130 mm), but in 1998 it rained only 48 mm in that month. On the other hand, the total precipitation during the months August, September and October 1998 was together 650 mm, which is almost the double compared to average of the earlier 16 years (320 mm).



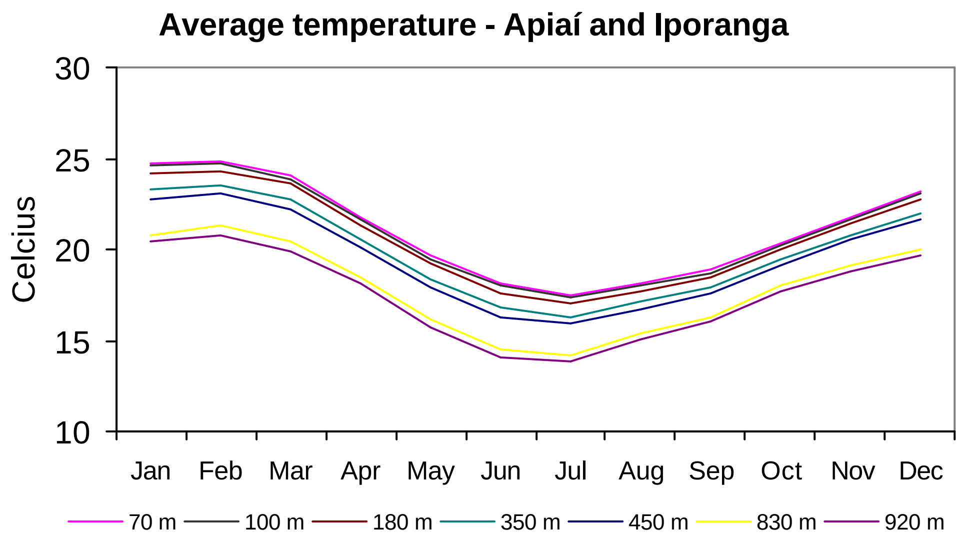


Figure 6: Monthly average (1972-1997) and monthly total precipitation (1998) in Bairro da Serra, PETAR (Pluviometric station Serra das Motas) and average temperature (1955) in Iporanga and Apiaí region[a].

Sampling sites

During the June expedition 16 sites were surveyed. The number of sites was reduced to 12 during the second trip due to weather and road conditions. Sites were selected according to river size, proximity to households, mines or agricultural fields, and also accessibility by car.

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[a] Source: Water and Electrical Energy Department of the State of São Paulo, DAEE.

Figure 8 shows the watersheds of Betari, Iporanga and Pilões Rivers and the selected sampling sites location.

The description of the sample sites is presented in Table 1. Latitude and longitude of each site was determined using a GPS receiver (Silva GPS Compass XL 1000 Forest). River depth and width were measured at different points in the stream section studied but only the averages are presented in that table. The classification of the flow speed was based on visual observation. The elevation was determined using topographical maps of the area (Instituto Brasileiro de Geografia e Estatística, 1987). The description of the kind of bedrock on which the streams flow was based on Shimada (1999).

Sites B6, B8, B9 and B11 were selected as controls (absence of known sources of contamination upstream). Site B6 is located at a tributary of the Furnas Stream and has no human influence except for a non-asphalt road, which is located in the vicinity. Site B8 is at the Couto Stream, approximately 50 meters from Couto Cave entrance. Site B9 is at Betari River, next to a camping area in Núcleo Santana. B11 is situated at one of the Betari tributaries, Passagem do Meio Stream.

Sites P2, P3, P4, P5, P6 and P7 are in streams located near agricultural areas. Site P2 is also close to a livestock farm. Information given by PETAR staff suggested that areas in the vicinity of P2 and P3 has been used for agricultural purposes, but not during the 2 or more years previously to the sampling campaign. Farms near P3 cultivated crops in 1997.

Sites I1 and I2 are located in the vicinity of Purical, a limestone mine. Site I4 is located in Iporanga River downstream to the confluence with a stream that receives particles from a limestone mine. Sites B4 and B5 are located in the Furnas River downstream a former lead-zinc-silver mine. Site B1 is located in the Betari River, downstream the Furnas confluence. Samples from site B7 were taken in the Monjolos Stream, which is located downstream Bairro da Serra village. Sites P1 and I3 are located next to small human settlements composed only by few houses. Sites B3 and B10 are located in the Betari River, downstream Bairro da Serra and the Furnas confluence.

Betari and Iporanga Rivers flow through areas of metasandstones, metaritmites, metacarbonates (marble, metalimestone and metadolomite) and phyllites upstream the sample sites B1, B3, B9, B10 and I4 (Figure 9). Furnas Stream flows on metacarbonates (B4, B5 and

B6), crossing a zone of phyllites between the first and the last sites; Monjolos (B7) and Couto (B8), on marble with intercalations of phyllites, metasiltites and schists; and Passagem do Meio (B11), on phyllites. Sample sites situated at Iporanga River headwaters are located on marble (I1 and I2) or granite bedrock (I3). Sample sites located at Pilões River headwaters are located on metasandstone with intercalations of phyllites (P1, P2 and P5), granite (P3) and marble (P4, P6 and P8). Sample site P7, located close to the Pilões River mouth, is situated on slates and phyllites associated to basic and acidic metavolcanic rocks.

Figure 7 is a schematic representation of sample sites distribution. For a better description of the sample sites, including marginal vegetation, human impacts and bed material, turbidity, and percentage of shading on the rivers, see Molander and Moraes (1998), and Moraes and Molander (1999).

The daily rainfall during the period of both field campaigns and the name of the sample station surveyed in each day are presented on Figure 10.

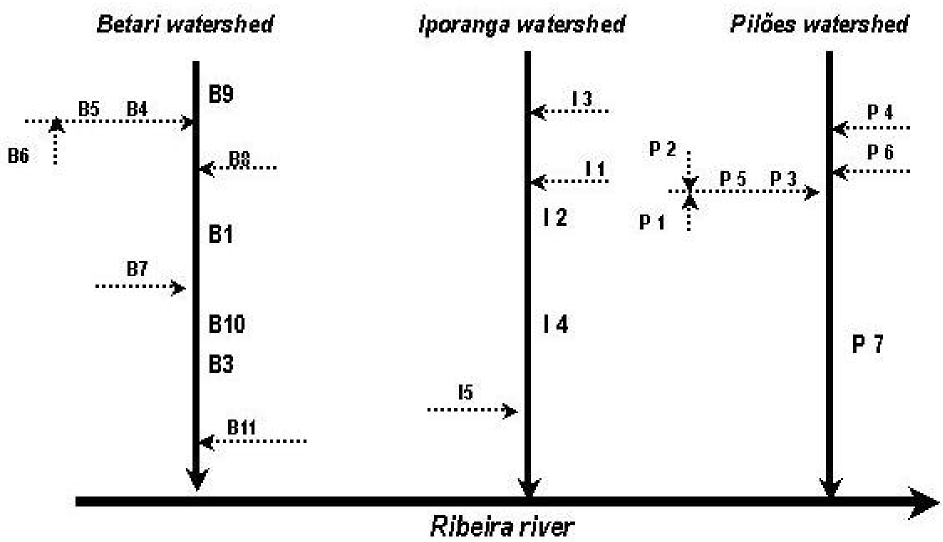

Figure 7: Schematic representation of sample sites location.

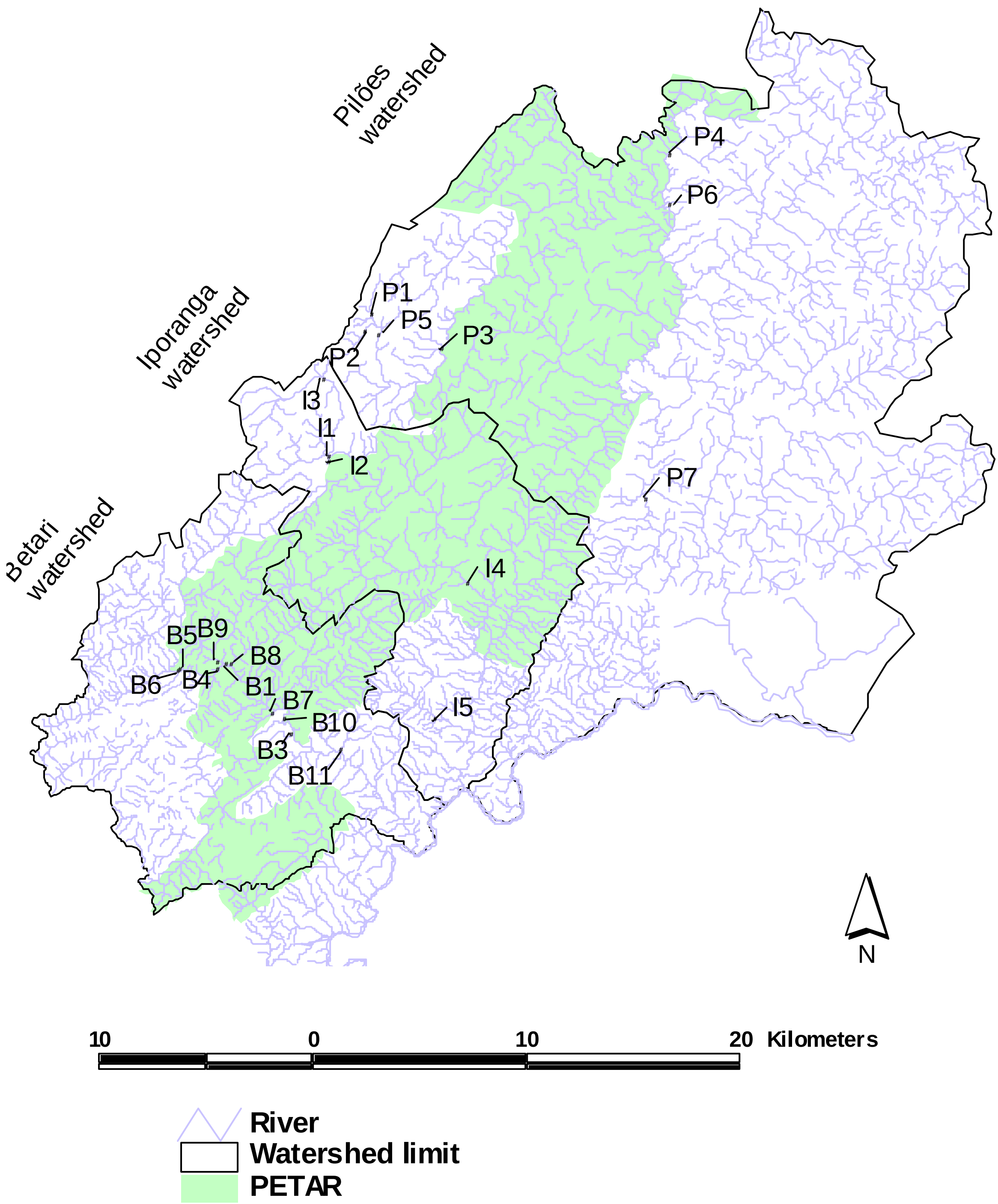

Figure 8: Schematic map of the study area showing sample sites location in Betari, Iporanga and Pilões watershed.

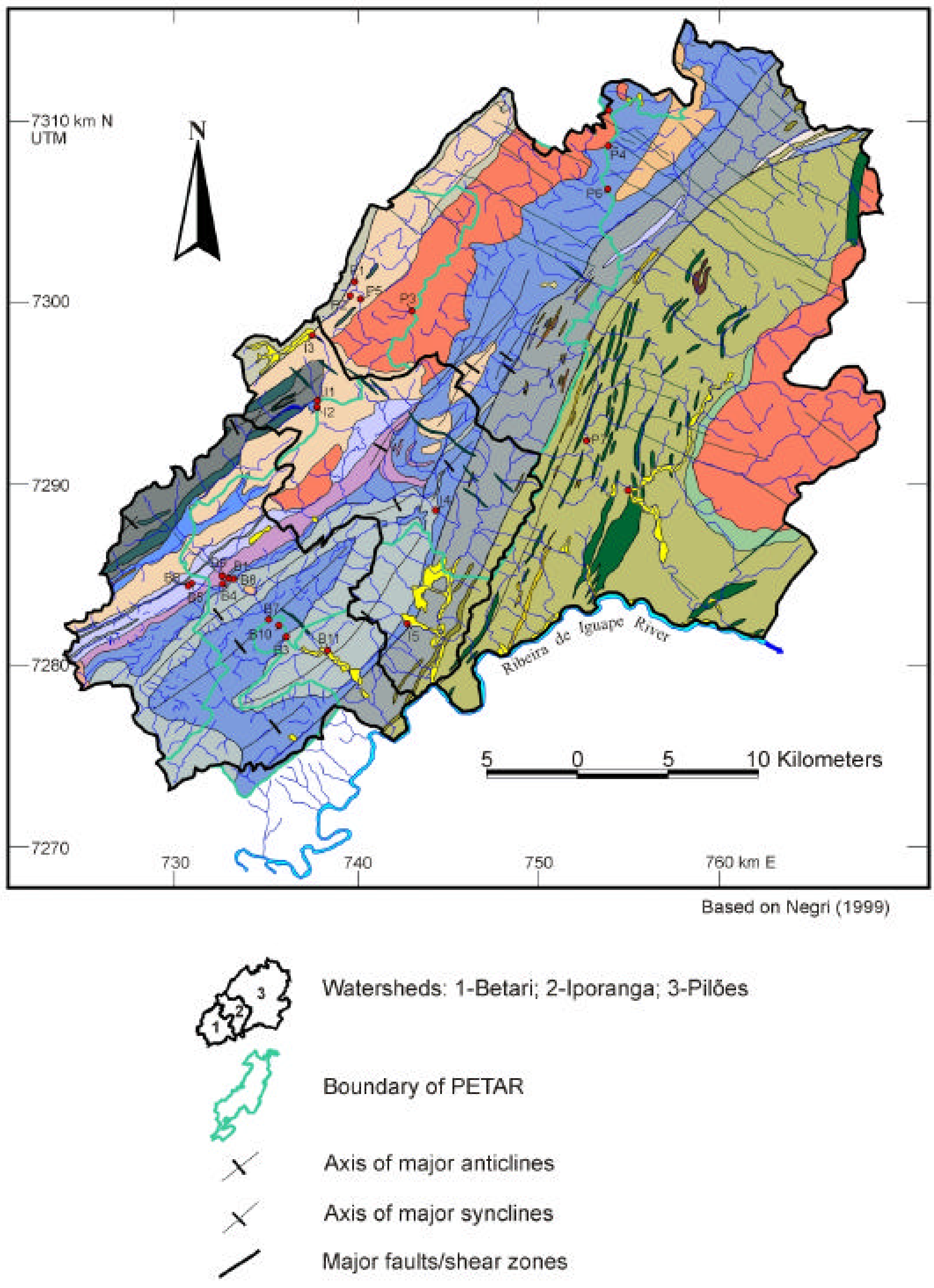

Figure 9: Schematic map of the study area showing lithostatgraphic units and sample sites location in Betari, Iporanga and Pilões watershed[a].

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[a] Sources: (Instituto Brasileiro de Geografia e Estatística, 1987) (Instituto Brasileiro de Geografia e Estatística, 1987; Negri, 1999)

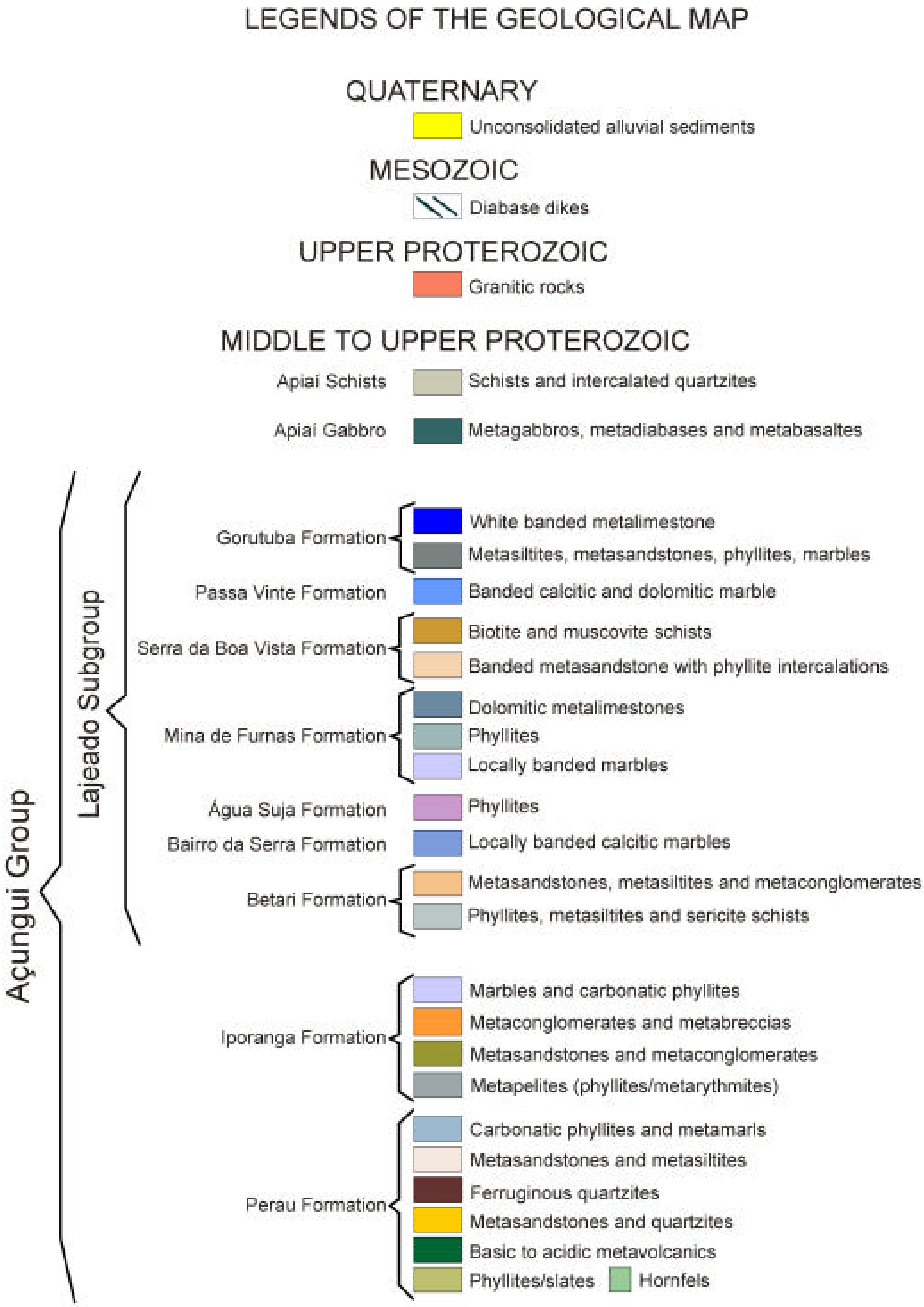
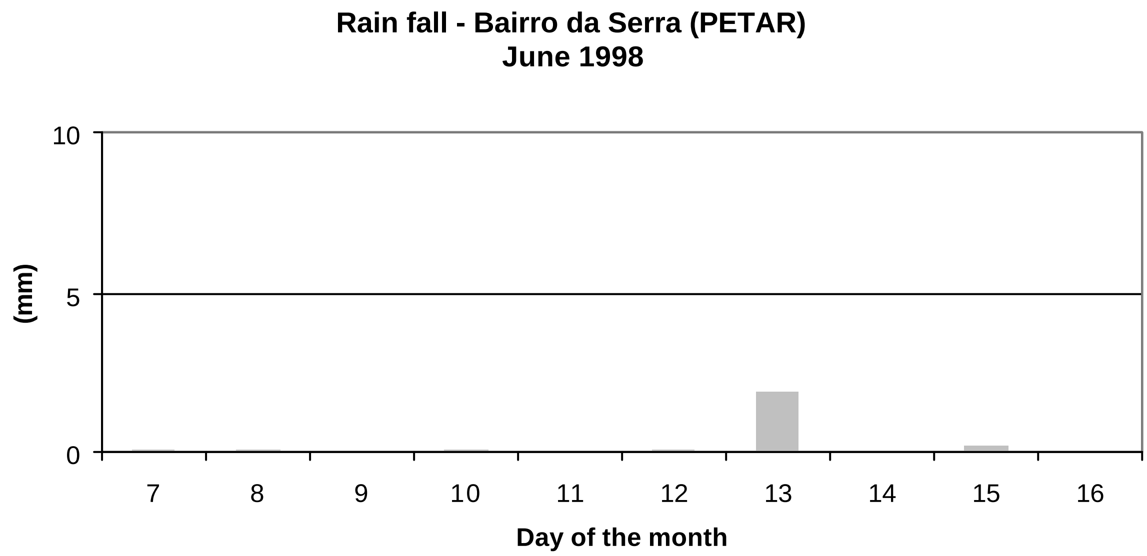

LEGENDS OF THE GEOLOGICAL MAP
QUATERNARY
Unconsolidated alluvial sediments
MESOZOIC
Diabase dikes
UPPER PROTEROZOIC
Granitic rocks
MIDDLE TO UPPER PROTEROZOIC
Apiai Schists
Schists and intercalated quartzites
Apiai Gabbro
Metagabbros, metadiabases and metabasaltes
Açungui Group
Lajeado Subgroup
Gorutuba Formation
White banded metalimestone
Metasiltites, metasandstones, phyllites, marbles
Passa Vinte Formation
Banded calcitic and dolomitic marble
Serra da Boa Vista Formation
Biotite and muscovite schists
Banded metasandstone with phyllite intercalations
Mina de Furnas Formation
Dolomitic metalimestones
Phyllites
Locally banded marbles
Água Suja Formation
Phyllites
Bairro da Serra Formation
Locally banded calcitic marbles
Betari Formation
Metasandstones, metasiltites and metaconglomerates
Phyllites, metasiltites and sericite schists
Iporanga Formation
Marbles and carbonatic phyllites
Metaconglomerates and metabreccias
Metasandstones and metaconglomerates
Metapelites (phyllites/metarythmites)
Perau Formation
Carbonatic phyllites and metamarls
Metasandstones and metasiltites
Ferruginous quartzites
Metasandstones and quartzites
Basic to acidic metavolcanics
Phyllites/slates
Hornfels

Table 1:Location and description of the sampling sites.

Watershed	Site	Name	Longitude W	Latitude S	Elevation	Width (m)	Depth (m)	Flow	Bedrock	Sampling datum	
										Jun 1998	Nov 98
Betari	B1	Betari River	48,699	24,533	240	10,0	0,4	Median	Marble/phyllite	8	20
Betari	B3	Betari River	48,668	24,562	240	10,0	0,5	Median	Marble/phyllite	13	
Betari	B4	Furnas Stream	48,703	24,536	260	4,0	3,5	Median	Metalimestone	11	18
Betari	B5	Furnas Stream	48,719	24,535	460	1,0	0,2	Median	Metalimestone	13	
Betari	B6	Furnas tributary	48,722	24,536	540	1,0	0,2	Median	Metalimestone	13	
Betari	B7	Monjolos Stream[a]	48,678	24,554	200	1,0	0,5	Median	Marble/phyllite	14	15
Betari	B8	Couto Stream	48,699	24,539	280	1,5	0,5	Median	Marble/phyllite	14	
Betari	B9	Betari River	48,703	24,532	260	10,0	0,5	Median	Marble/phyllite	16	18
Betari	B10	Betari River	48,672	24,556	200	15,0	0,4	Median	Marble/phyllite		13
Betari	B11	Passagem do Meio Stream	48,646	24,568	120	3,0	0,4	Median	Phyllite		20
Iporanga	I1	Iporanga tributary	48,656	24,445	700	2,5	0,4	Median	Marble	9	
Iporanga	I2	Iporanga River	48,654	24,448	700	0,3	7,0	Slow	Marble	9	19
Iporanga	I3	Iporanga tributary	48,657	24,412	840	2,5	1,0	Slow	Metasandstone	10	16
Iporanga	I4	Iporanga river	48,589	24,498	160	11,0	0,4	Median	Phyllite	11	14
Pilões	P1	Polões tributary	48,634	24,496	840	0,6	0,1	Slow	Metasandstone	10	
Pilões	P2	Pilões triburaty	48,638	24,380	860	1,0	0,4	Slow	Metasandstone	10	
Pilões	P3	Timimina Stream	48,604	24,398	840	5,0	1,0	Slow	Granite	12	
Pilões	P4	Pilões River	48,500	24,315	720	5,0	1,0	Slow	Marble/phyllite	12	
Pilões	P5	Córrego Preto Stream	48,632	24,393	900	2,0	0,6	Slow	Metasandstone		16
Pilões	P6	Pilões triburaty	48,501	24,337	760	8,0	0,5	Slow	Marble/phyllite		17
Pilões	P7	Pilões River	48,507	24,461	140	30,0	0,5	Median	Slate/phyllite		21

[a] Also known as Jaguatirica Stream according to the Instituto Brasileiro de Geografia e Estatística (1987).



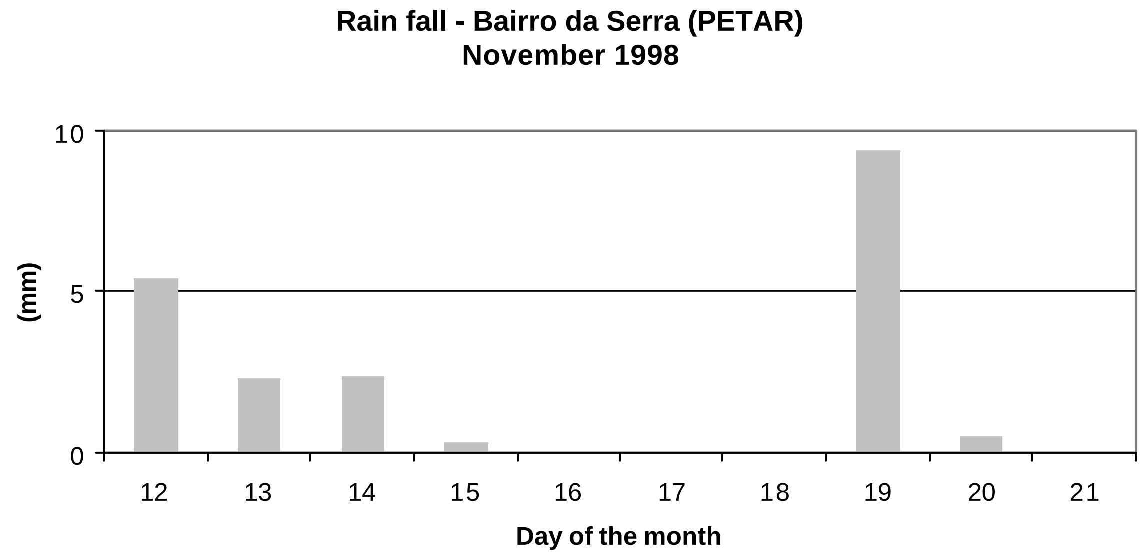


Figure 10: Daily rainfall during the sampling campaigns in June and November 1998 and sampling station surveyed in each day.

Selected parameters

During this study the concentration of nitrogen and phosphorus in different forms (as nitrate, ammonia, total nitrogen, phosphate and total phosphorus) were measured. Since interaction among different water parameters may affect nutrient availability, other abiotic factors also were measured. They included temperature, pH and alkalinity.

Nitrogen is available for uptake by plants and bacteria as nitrate, ammonia and urea. During the decomposition of organic material, ammonium (NH_3) is formed. In the nitrification process, ammonium is oxidised to nitrate (NO_3^-) by bacteria in an aerobic environment. If the oxygen level is low, the end product will be the middle step nitrite (NO_2^-) in stead. During conditions with low levels of oxygen, the nitrate present can also be reduced to nitrite. In totally anaerobic conditions, the bacterial denitrification process reduces nitrite and nitrate to nitrogen gas and the nitrogen can leave the water phase (Bydén *et al.*, 1996). Ammonia is normally present in low concentrations in water and soil. This is both due to that it is bound to particles and to that it is oxidised to nitrate if the oxygen concentration is high. Nitrate is therefore the most common form of plant available nitrogen.

Phosphorus appears in mineral form, water phase and biological tissue (Swedish Environmental Protection Agency, 1993). In natural waters, the plant available forms of phosphorus are the inorganic orthophosphates, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. They are together called phosphate-phosphorus (PO_4-P). The total amount of phosphorus in a stream is a potential nutrient source, since there are a number of processes (e.g., change in pH) that can transform it into orthophosphates (Bydén *et al.*, 1996). Phosphate can appear bound to different molecules, such as iron hydroxide complexes or aluminium hydroxides and during certain conditions it can be released as the plant available phosphate ion (PO_4^{3-}). Such conditions can for instance be a high pH or lack of oxygen (Swedish Environmental Protection Agency, 1993).

The pH value is described as the negative logarithm of the concentration of hydrogen ions, which is expressed on a scale from 0 to 14 (0 is an extremely acid water and 14 is extremely basic). Alkalinity describes the buffering capacity of water, e.g., its capability to neutralize acids, that is its ability to accept hydrogen ions without responding with a decrease in pH (Bydén et al., 1996).

As mentioned before, the breakdown of organic compounds present in sewage sludge or run off from anthropogenic fields may cause a decrease of oxygen concentrations in water. Therefore, the concentration of dissolved oxygen (DO), as well as the chemical demand of oxygen (COD) was measured at each sampling station.

Other characteristics of the watercourses may be affected by the input of nutrients. For instance, nutrient rich waters have a greater conductivity than nutrient poor waters (Bydén et al., 1996). In addition, the concentration of nitrate and phosphate can influence the hardness of the water, which is defined as the sum of the salts that is built up by calcium, magnesium, strontium and barium in combination with carbonate, sulphate, chloride, nitrate and phosphate (Bydén et al., 1996). For that reason, both hardness and conductivity were measured during this study.

Methodology

Conductivity, pH, dissolved oxygen and temperature were all measured in the streams at the sampling stations by a multipurpose instrument (Horiba U-10 Water Quality Checker).

Nitrate, phosphate, hardness and alkalinity were measured in a temporary laboratory at one of the houses in PETAR using a Hach DR/700 (June) or DR/2010 (November) Portable Colorimeter. Water samples were collected and stored in plastic bottles no longer than 12 hours before analysis.

Water samples (3 plastic bottles, 50 ml, from each sampling site) were acidified with 0.2 ml of H_2SO_4 (9 M), frozen and later transported to Sweden. The concentrations of total nitrogen, total phosphorus and ammonia, and chemical demand of oxygen were measured at the laboratory of the Department of Sanitary Engineering at Chalmers University of Technology.

Table 2 shows methodology and instruments used for analysis of different parameters and number of samples. See Appendix for a detailed description of analysis techniques.

Possible sources of errors

The Horiba Water Checker was not properly used during the first days of the campaign in June (sites I1, I3, P1 and P2). The electrode was put into a beaker filled with sample water, instead of being plunged directly into the river or stream as the method prescripts. Therefore DO measurements from those sites had to be excluded. Regarding pH, the measurements taken in the beaker show a slightly higher value than the ones taken directly in the water. The errors were judged to be relatively small and were not excluded in the analysis. The values of conductivity and temperature were not affected by the different ways of measuring. This was verified by control measurements in both ways at a number of sample sites.

Other possible sources of error are related to the sample storage and transportation, and calibration of the equipments

Table 2. Selected parameters, methods and nu mber of sampling sites and replicates.

Parameter	Instrument	Method	Range	Resolution	Local of analysis	Number of replicates per site	
						Jun 98	Nov 98
pH	Horiba	Electrode	0-14	0.1	Field	3	3
Temperature	Horiba	Thermometer	0-50 ^{o}C	0.1 ^{o}C	Field	3	3
Dissolved Oxygen (OD)	Horiba	Electrode	0-19.9 mg/L	0.01 mg/L	Field	3	3
Conductivity	Horiba	Electrode	0-100 mS	0.01 mS	Field	3	3
Hardness		Titration			PETAR lab	1	3
Alkalinity		Orion Total Alkalinity Test Kit	0-225 ppm $CaCO_3$	1 ppm	PETAR lab	0	3
Chemical Demand of Oxygen (COD)	Hach	Reactor Digestion	0-150 mg/L	1 mg/L	Chalmers lab	0	3
Nitrate	Hach	Cadmium reduction, Diazotization	0-0.5 mg/L $NO3^-$	0.01 mg/L	PETAR lab	3	3
Phosphate	Hach	PhosVer 3 (Ascorbic Acid)	0-2.50 mg/L $PO4^{3-}$	0.01 mg/L	PETAR lab	3	3
Total Nitrogen	Hach	TNT Persulfate Digestion	0-25 mg/L N	1 mg/L	Chalmers lab	3	3
Total Phosphorus	Hach	PhosVer 3 with Acid Persulfate Digestion	0-3.50 mg/L P	0.01 mg/L	Chalmers lab	3	3
Ammonia	Hach	Salicylate	0-1.00[a] or 0-0.50[b] mg/L NH_3-N	0.01 mg/L	Chalmers lab	1	3

[a] Hach DR/700

[b] DR/2010

Results

Chemical and physical water parameters

Temperature, pH, dissolved oxygen, hardness, conductivity, alkalinity, and chemical demand of oxygen measured in PETAR streams, during June and November 1998, are presented on Table 3.

Water temperature was lower in winter (June) than in summer (November). It ranged from 13,0-18,6 in June and 16,6 and 22,1 ^{o}C in November, as shown in Figure 11. Measurements of pH were also lower during winter (Figure 12). They ranged from 6,3-8,2 in June and 6,5-8,4 in November.

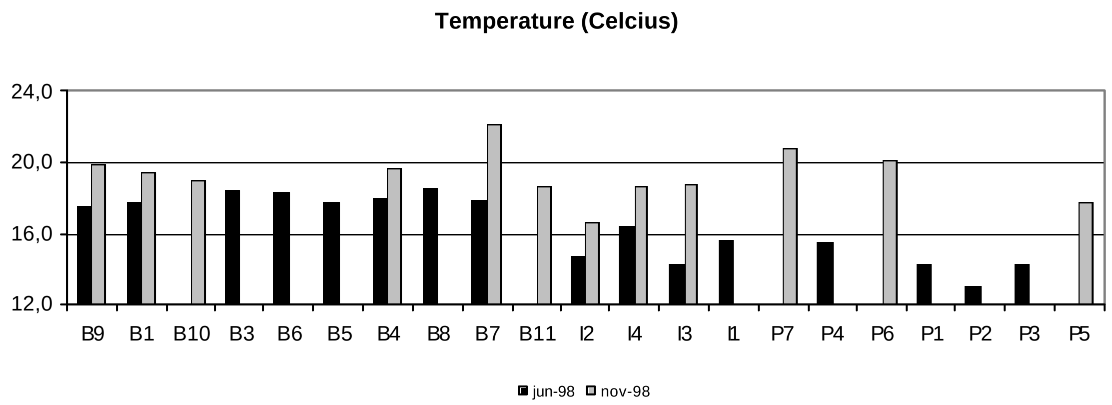


Figure 11: Measured water temperature in Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

[a] For each site only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

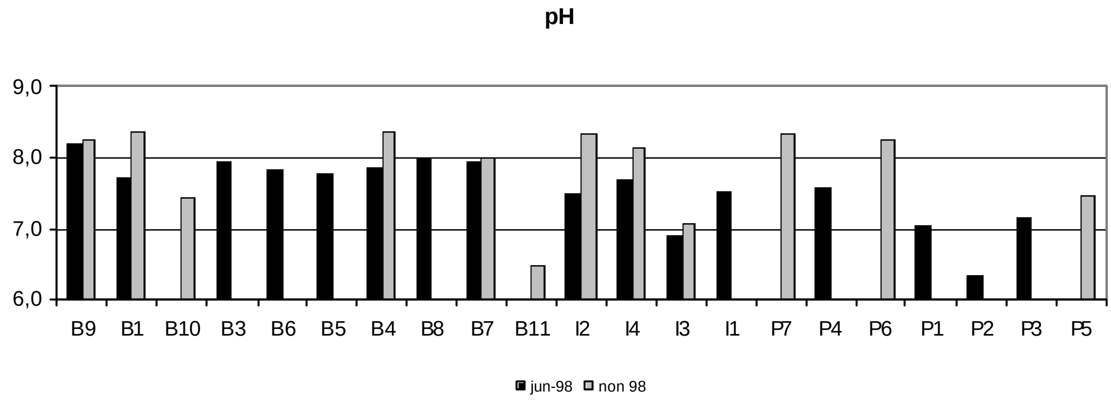


Figure 12: Measured pH in Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries [a,a].

Dissolved oxygen (DO) values were higher in winter compared to summer (Figure 13). DO concentration was higher in fast flow waters, e.g., in Betari (B9, B1, B3, B10), Iporanga (I4) and Pilões (P7) than in slow flowing streams, e.g., I3 and P5. High values for chemical oxygen demand (COD) were measured at B7, I3 and I2 (Figure 14).

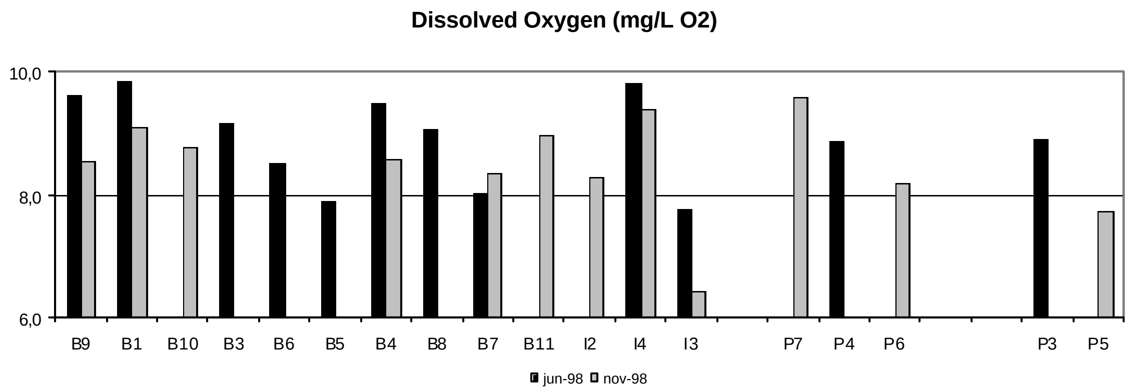


Figure 13: Measured dissolved oxygen in Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[b].

[a] Values below 7 indicate acid water and, above 7, basic water.

[b] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, I2, I1, P7, P6 and P1, P2 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

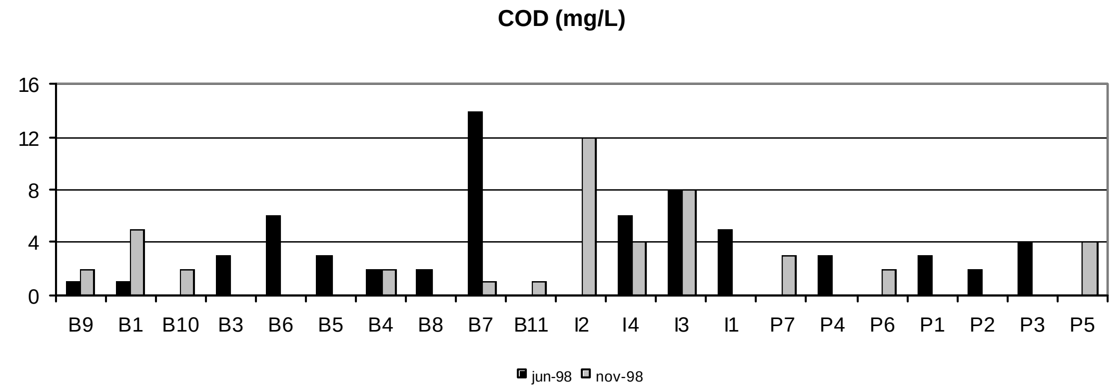


Figure 14: Measured chemical oxygen demand (COD) in Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

In general terms, conductivity values were lower in summer than in winter for the same sampling sites (Figure 15). The highest conductivity values were measured in Furnas River both upstream (B6) and downstream (B5 and B4) piles of waste rock from a non-active silver-lead-zinc-silver mine. High conductivity values were also detected at B7 (downstream Bairro da Serra). Passagem do Meio Stream (B11) and some of Pilões tributaries (P2, P3) presented a very low conductivity values.

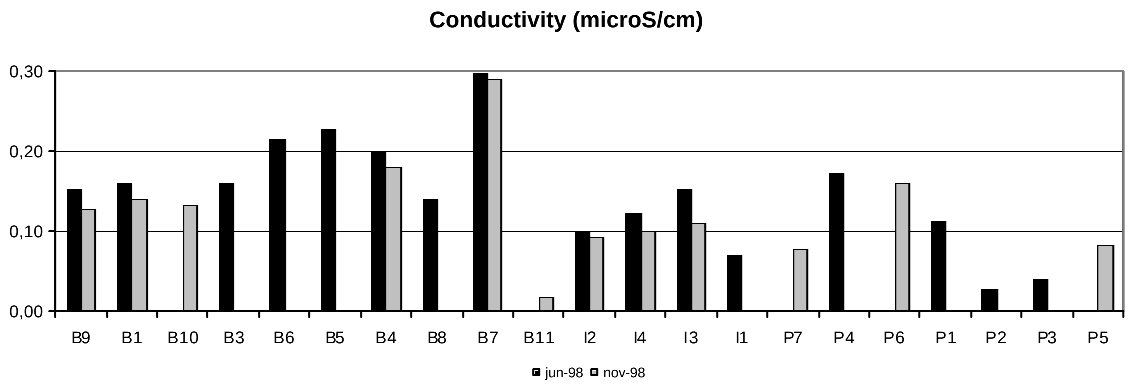


Figure 15: Measured conductivity in Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[b].

[a] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

[b] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

Most of sampled streams presented soft of very soft water. B4 and P6 presented medium hard water, and B7, hard water (Figure 16). Alkalinity was not measured during the first field trip (June 98). During the second field trip (November), Passagem do Meio Stream (B11) presented zero alkalinity, while the other streams presented values between 20 and 136 ppm Ca CO_3.

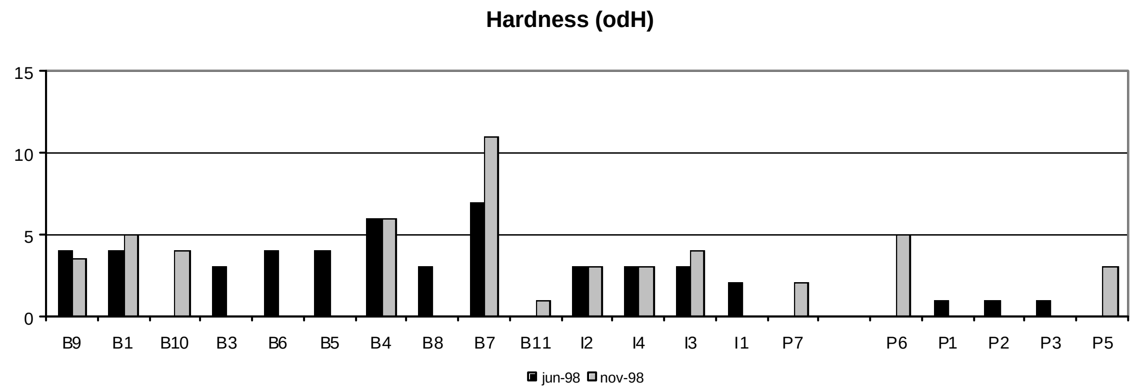


Figure 16: Measured hardness at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries [a].

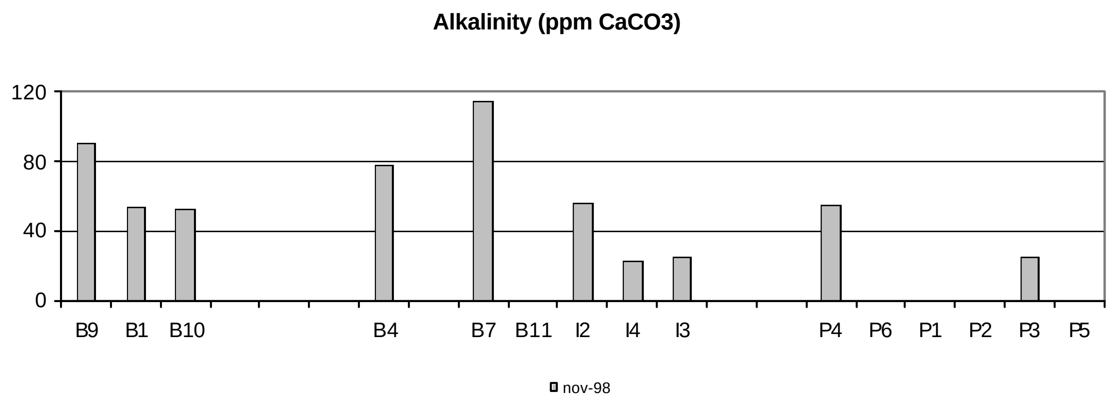


Figure 17: Measured alkalinity at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

[a] For each site, only one of three measurements is shown (the central value). No measurements during June 98; and at B3, B6, B5, B8, I1, P7, P4, P1, P2 and P3 in November 98.

Table 3: Water parameters in PETAR streams: Betari (B), Iporanga (I), Pilões (P) and their tributaries.

	Site	*T* (^oC)			*pH*			*DO* (*mg/L*)			*Conductivity* (*mS/cm*)			*Hardness* (^{o}*dH*)			*Alkalinity* (*ppm CaCO3*)			*COD* (*mg/L*)		
Jun 98	B9	17,5	17,5	17,5	8,20	8,20	8,24	9,51	9,63	9,65	0,153	0,153	0,153	4						0	1	7
	B1	17,7	17,8	17,9	7,72	7,72	7,73	9,84	9,84	9,93	0,158	0,159	0,160	4						1	1	6
	B3	18,4	18,5	18,5	7,85	7,92	8,02	8,89	9,16	9,35	0,158	0,159	0,159	3						1	3	6
	B6	18,3	18,4	18,4	7,82	7,83	7,90	8,41	8,52	8,59	0,214	0,214	0,214	4						3	6	15
	B5	17,7	17,7	17,7	7,73	7,78	7,83	7,69	7,88	8,00	0,226	0,227	0,227	4						1	3	10
	B4	18,0	18,0	18,1	7,82	7,86	7,91	9,38	9,49	9,84	0,198	0,199	0,200	6						2	2	3
	B8	18,5	18,6	18,6	8,00	8,01	8,03	8,85	9,06	9,23	0,140	0,140	0,140	3						0	2	4
	B7	17,9	17,9	17,9	7,88	7,92	7,95	7,77	8,01	8,35	0,297	0,297	0,297	7						8	14	16
	I2	14,7	14,7	15,4	7,37	7,50	7,52				0,085	0,101	0,102	3						0	0	5
	I4	16,4	16,4	16,5	7,66	7,69	7,76	9,81	9,82	9,78	0,124	0,124	0,124	3						0	6	7
	I3	14,2	14,2	14,3	6,85	6,88	6,92	7,64	7,74	7,76	0,152	0,152	0,152	3						5	8	13
	I1	15,5	15,8	17,1	7,52	7,52	7,58				0,071	0,071	0,084	2						3	5	
	P4	15,4	15,4	15,5	7,55	7,59	7,61	8,83	8,86	8,91	0,172	0,172	0,172							2	3	7
	P1	14,2	14,3	14,4	7,04	7,05	7,08				0,110	0,112	0,112	1						0	3	0
	P2	13,0	13,4	15,1	6,30	6,33	6,37				0,026	0,027	0,027	1						2	2	4
	P3	14,2	14,3	14,3	7,06	7,15	7,20	8,85	8,90	9,00	0,040	0,041	0,041	1						4	4	7
Nov 98	B9	19,8	19,7	19,8	8,24	8,25	8,23	8,51	8,54	8,63	0,128	0,128	0,128	3	4	4		91	136	1	2	3
	B1	19,4	19,4	19,4	8,32	8,36	8,36	9,02	9,10	9,16	0,140	0,140	0,140	5	5	6	53	53	55	2	5	7
	B10	19,0	19,0	19,0	7,35	7,42	7,46	8,73	8,78	8,81	0,133	0,133	0,133	4	4	4		52		1	2	3
	B4	19,6	19,6	19,7	8,28	8,35	8,37	8,49	8,59	8,69	0,181	0,181	0,181	5	6	6	77	77	79	2	2	3
	B7	22,1	22,1	22,0	7,97	7,98	8,01	8,27	8,33	8,26	0,289	0,289	0,290	10	11	11	111	115	117	0	1	4
	B11	18,6	18,6	18,7	6,49	6,49	6,53	8,94	8,96	8,94	0,017	0,017	0,017	1	1	1	0	0	0	0	1	2
	I2	16,6	16,6	16,6	8,30	8,32	8,32	8,28	8,28	8,35	0,094	0,094	0,094	2	3	3	55	56	56	11	12	15
	I4	18,6	18,6	18,7	8,15	8,15	8,17	9,35	9,39	9,40	0,100	0,100	0,101	3	3	3	16	23	27	2	4	4
	I3	18,7	18,7	18,8	6,99	7,06	7,08	6,33	6,42	6,46	0,110	0,111	0,111	3	4	5	20	25	27	4	8	10
	P7	20,8	20,7	20,8	8,29	8,32	8,32	9,59	9,57	9,65	0,078	0,079	0,079	2	2	2				2	3	6
	P6	20,1	20,1	20,2	8,26	8,26	8,27	8,15	8,17	8,25	0,158	0,159	0,160	4	5	5	53	55	56	0	2	6
	P5	17,8	17,7	17,8	7,44	7,46	7,42	7,82	7,73	7,88	0,083	0,083	0,084	3	3	4	21	25	24	1	4	11
	P5	17,8	17,7	17,8	7,44	7,46	7,42	7,82	7,73	7,88	0,083	0,083	0,084	3	3	4	21	25	24	1	4	11

Nutrient concentrations

Nutrient concentration (nitrate, ammonia, total nitrogen, phosphate and total phosphorus) measured in PETAR streams, during June and November 1998, is presented in Table 4.

The highest concentrations of nitrate were found in Betari (B9, B1 and B3), in its tributaries (B4, B8 and B11) and in Iporanga River (I4) as showed on Figure 18. The highest values of ammonia (Figure 19) were measured at B7 in June, and I2 in November. Total nitrogen concentration was also high at those two sites (I2 and B7), but also in B8 (Figure 20).

The highest concentrations of phosphate were found at B7 and P4 in June (Figure 21). The highest concentrations of total phosphorus were at B7 and P4 during November (Figure 22).

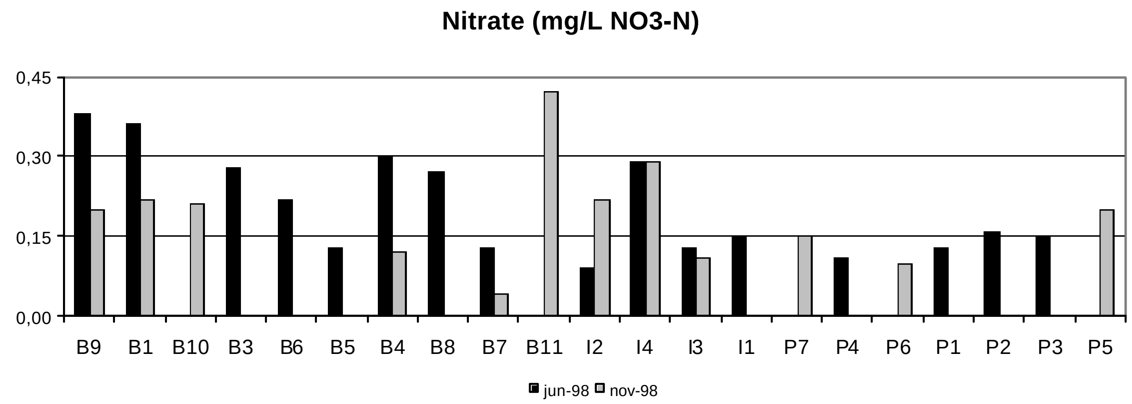


Figure 18: Measured nitrate concentrations at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

[a] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P4, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

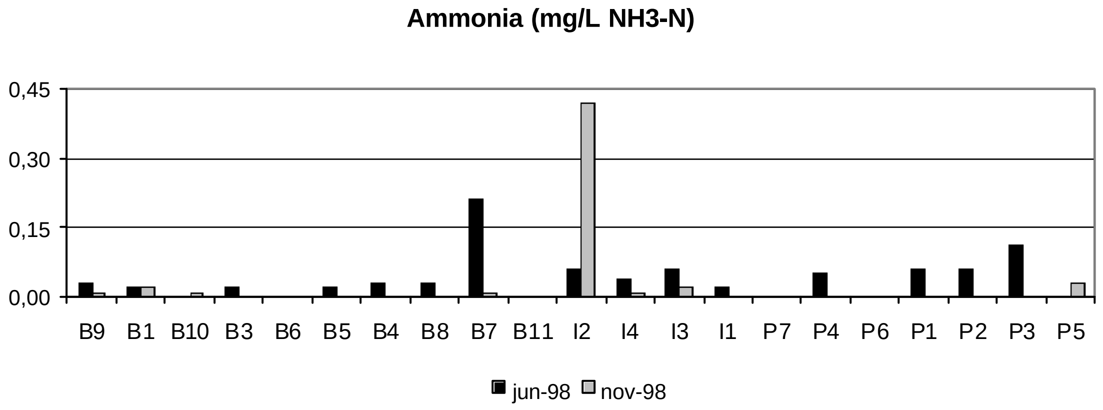


Figure 19: Measured ammonia concentrations at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries [a].

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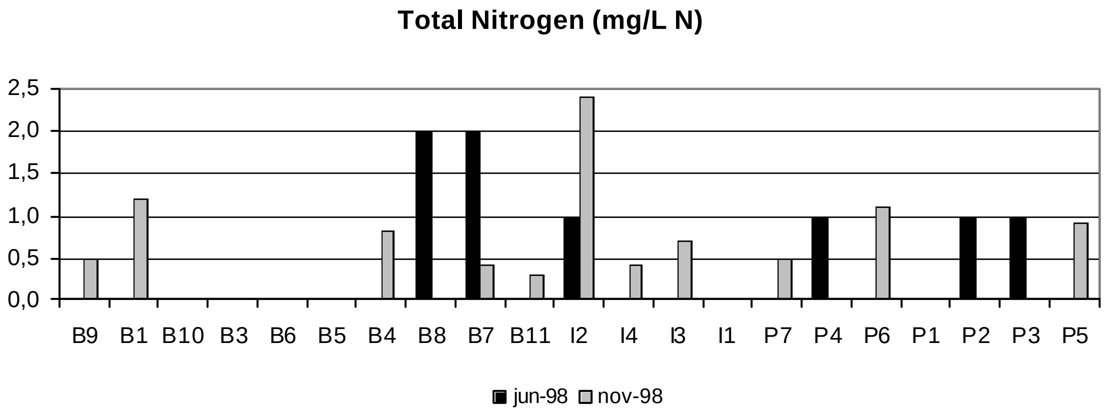

Figure 20: Measured total nitrogen concentrations at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

[a] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P4, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98.

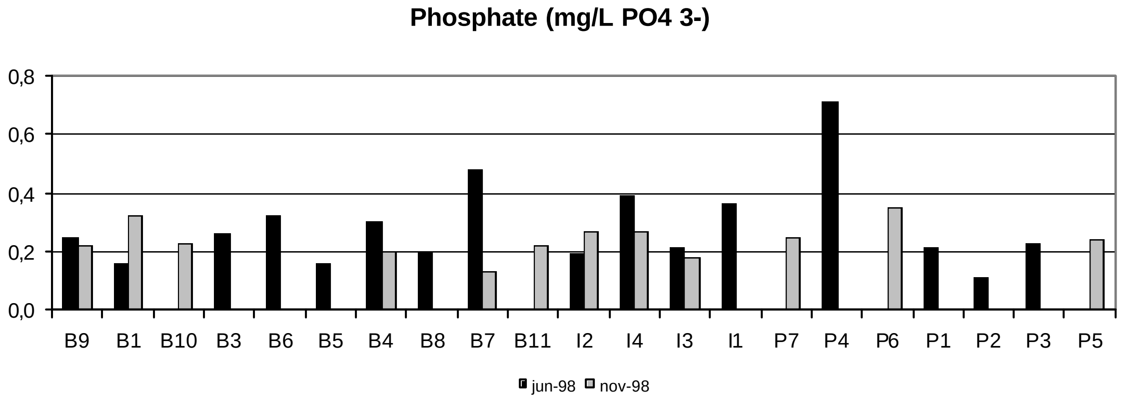

Figure 21: Measured phosphate concentrations at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries [a].

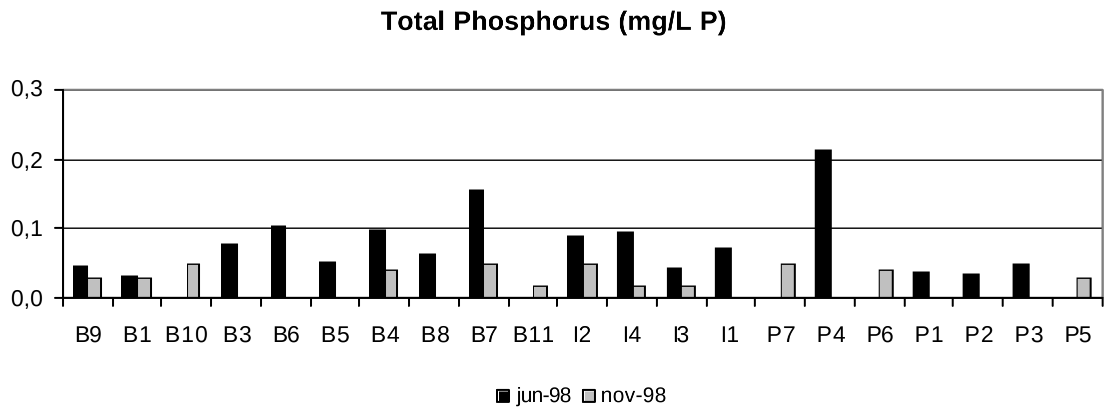

Figure 22: Measured total phosphorus concentrations at Betari (B), Iporanga (I) and Pilões (P) Rivers and their tributaries[a].

[a] For each site, only one of three measurements is shown (the central value). No measurements at B10, B11, P7, P4, P6 and P5 during June 98; and at B3, B6, B5, B8, I1, P4, P1, P2 and P3 in November 98

Table 4: Nutrient concentration in PETAR streams: Betari (B), Iporanga (I), Pilões (P) and their tributaries.

	Site	Nitrate (mg/L NO_3-N)			Ammonia (mg/L NH_3-N)			Total nitrogen (mg/L N)			Phosphate (mg/L PO_4^{3-})			Total phosphorus (mg/L P)		
June 98	B9	0,27	0,38	0,41	0,03			0	0	0	0,14	0,25	0,29	0,09	0,05	0,08
	B1	0,30	0,36	0,40	0,02			0	0	1	0,10	0,16	0,19	0,05	0,03	0,06
	B3	0,24	0,28	0,29	0,02			0	0	2	0,24	0,26	0,31	0,08	0,08	0,10
	B6	0,16	0,22	0,25	0,00			0	0	1	0,29	0,32	0,34	0,09	0,10	0,11
	B5	0,13	0,13	0,14	0,02			0	0	0	0,13	0,16	0,32	0,04	0,05	0,10
	B4	0,27	0,30	0,37	0,03			0	0	0	0,20	0,30	1,17	0,07	0,10	0,38
	B8	0,24	0,27	0,35	0,03			1	2	5	0,19	0,20	0,25	0,06	0,07	0,08
	B7	0,12	0,13	0,13	0,21			2	2	4	0,42	0,48	0,57	0,14	0,16	0,19
	I2	0,08	0,09	0,17	0,06			0	1	1	0,28	0,19	0,16	0,06	0,09	0,05
	I4	0,26	0,29	0,33	0,04			0	0	1	0,29	0,39	0,12	0,13	0,09	0,04
	I3	0,10	0,13	0,14	0,06			0	0	1	0,13	0,21	0,13	0,07	0,04	0,04
	I1	0,12	0,15	0,15	0,02			0	0	1	0,23	0,36	0,35	0,12	0,07	0,11
	P4	0,09	0,11	0,11	0,05			1	1	1	0,65	0,71	0,58	0,19	0,21	0,23
	P1	0,13	0,13	0,20	0,06			0	0	0	0,12	0,21	0,12	0,04	0,04	0,07
	P2	0,12	0,16	0,17	0,06			1	1	1	0,09	0,11	0,12	0,03	0,04	0,04
	P3	0,15	0,15	0,16	0,11			1	1	2	0,15	0,23	0,15	0,07	0,05	0,05
Nov 98	B9	0,14	0,20	0,24	0,01	0,01	0,01	0,3	0,5	1,0	0,19	0,22	0,32	0,01	0,03	0,03
	B1	0,20	0,22	0,30	0,01	0,02	0,03	0,4	1,2	1,5	0,24	0,32	0,45	0,03	0,03	0,06
	B10	0,17	0,21	0,30	0,01	0,01	0,02	0,0	0,0	0,4	0,13	0,23	0,32	0,00	0,05	0,05
	B4	0,09	0,12	0,12	0,00	0,00	0,01	0,6	0,8	1,3	0,09	0,20	0,35	0,04	0,04	0,04
	B7	0,03	0,04	0,04	0,00	0,01	0,03	0,4	0,4	0,6	0,07	0,13	0,20	0,04	0,05	0,05
	B11	0,41	0,42	0,44	0,00	0,00	0,00	0,1	0,3	0,7	0,12	0,22	0,37	0,01	0,02	0,04
	I2	0,16	0,22	0,27	0,40	0,42	0,46	1,7	2,4	5,0	0,19	0,27	0,27	0,04	0,05	0,12
	I4	0,27	0,29	0,30	0,01	0,01	0,03	0,2	0,4		0,14	0,27	0,27	0,02	0,02	0,04
	I3	0,10	0,11	0,12	0,02	0,02	0,04	0,1	0,7	8,0	0,11	0,18	0,34	0,01	0,02	0,04
	P7	0,15	0,15	0,19	0,00	0,00	0,02	0,2	0,5	1,2	0,11	0,25	0,30	0,03	0,05	0,05
	P6	0,07	0,10	0,13	0,00	0,00	0,00	0,3	1,1	1,4	0,21	0,35	0,38	0,04	0,04	0,06
	P5	0,19	0,20	0,21	0,02	0,03	0,03	0,2	0,9	1,1	0,15	0,24	0,55	0,03	0,03	0,40

Discussion

According to Semkin *et al.* (1994), most of the seasonal variations in stream water chemistry are related to climate (e.g. evaporation, precipitation, temperature) and biotic factors (e.g., nutrient assimilation, mineralization, nitrification, production of organic acids, transpiration). Therefore, they are largely driven by processes taking place in the terrestrial part of the catchment. Seasonal variation could be observed in some of the parameters measured in PETAR streams. Dissolved oxygen and conductivity seem to be higher in winter than during summer. On the other hand, pH values are lower in winter than in summer.

The physical characteristics and chemical composition of stream water can also vary substantially in a short-term. This can happen for instance after prolonged heavy rains (typical during summer season in PETAR region), which will increase the run off from land. Common variations include decline in alkalinity and pH Semkin *et al.* (1994). Each site was sampled only once in each field campaign, since the present study aimed to indicate the range of seasonal and spatial variability. However, some of the results can be partly explained by short-term variation. For instance, observed differences in temperature among the sites during the same sampling campaign can be due to weather conditions and sampling time, besides other factors such as size of the river, shading, distance of the sample site to caves and elevation above the sea level.

Spatial variation of chemical parameters is also expected within the same catchment area. It can be related to many natural factors, such as, elevation, bedrock characteristics, riverbed structure, marginal vegetation, etc. For instance, high values of pH were expected in PETAR region since most of the rivers flow on carbonatic rocks (marble, metalimestone and metadolomite). On the other hand, low pH values can occur near granite or phyllite regions. Those low values can also result from the occurrence of sulfides in the bedrock (mostly pyrite in this case), which acidify water when decomposed. In addition to the natural factors, anthropogenic activities such as discharge of domestic sewage and agriculture can partly explain the spatial variability of the chemical stream water characteristics.

Large rivers such as Betari, Iporanga and Pilões (sample sites B9, B1, B10, B3, I4 and P7) presented similar values of pH, DO, conductivity and hardness. However, large differences in chemical parameters could be observed among small streams, even inside the same catchment area. For instance, water samples from Furnas (B6, B5 and B4), Couto (B8) and Monjolos (B7) Streams were basic, soft or medium hard and presented, relatively, high alkalinity and conductivity. On the other hand, water samples from Passagem do Meio Stream (B11) were slightly acid, very soft, had zero alkalinity and very low conductivity. Those differences are probably reflecting bedrock characteristics.

During November 1998, relatively high concentrations of ammonia and total nitrogen and high chemical demand of oxygen were observed at the headwaters of Iporanga River at site I2. A very high concentration of suspended particles was also observed during the day of sampling, which increased the water turbidity considerably. That was probably a result of discharges from Purical, a limestone mine industry. Since TNT is often used for exploding limestone rocks, the mine can cause increase of nitrogen in the stream. Nevertheless, other possible sources of nitrogen such as sewage discharge should also be taken into consideration since human settlements are found upstream this mine.

Relatively high concentrations of phosphorus and phosphate were also observed in the headwaters of Pilões River (P4) during November 1998. Agricultural activities in the area may be a source of phosphorus in that case.

During June 1998, high concentrations of ammonia, phosphate and total phosphorus and high COD were observed in Monjolos Stream in comparison to other surveyed sites inside Betari watershed. In that stream, algae and macrophyta biomass were abundant. Such conditions are likely to be consequences of discharges of sewage from the village of Bairro da Serra. However, those discharges do not seem to increase the concentration of nutrients in Betari River downstream Monjolos (B3) convergence due to dilution of contaminants. Such high concentrations were however not observed in Monjolos Stream during the second field trip when the same parameters were measured.

Conclusion

Seasonal variation in PETAR stream water chemistry can be explained by climate and biotic factors. Spatial variability can be largely elucidated by natural factors, such as bedrock characteristics and flow velocity. However, anthropogenic factors can also be locally affecting stream quality. At the headwaters of Iporanga and Pilões Rivers an increase in inorganic nutrients concentration (nitrogen and phosphorus respectively) was observed. That can be a consequence of discharge of domestic sewage, fertilizers application in agriculture or even use of explosives containing nitrogen in mining activities. Indication of early stages of eutrophication (observed increase in plant biomass, measured increase in nutrients availability and chemical demand of oxygen) was found in Monjolos Stream downstream outlets of domestic sewage from the village of Bairro da Serra.

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Appendix

Description of the methods applied for analysis of stream water physical and chemical parameters:

Temperature, pH, Conductivity, DO

Equipment: Horiba Water Quality Checker U-10. The measurements were carried out in the field by immersing the analysis device directly in water. *Measurement principles*: pH: glass electrode method; conductivity-exchange electrode method; dissolved oxygen: membrane galvanized battery method; temperature: thermistor method. *Measure ranges*: pH: 0pH ~ 14pH; conductivity: 0mS/cm ~ 100mS/cm; dissolved oxygen: 0mg/l ~ 19.9mg/l; temperature: 0¡C ~ 50¡C; Repeatability: pH: ±0.05¡C; conductivity: ±1.0% F.S.; dissolved oxygen: ±1mg/l; temperature: ±3¡C; *Temperature compensation range*: pH: ±0°C-50°C; conductivity: ±0°C-50°C; dissolved oxygen (Horiba Water Quality Instrument).

Alkalinity

Equipment: Orion Total Alkalinity Test Kit (Onion Research Incorporated).

Hardness

Equipment: Aquanal-Plus, Complex Formation Method based on titration. *Summary of Method:* Using two reagents, the basis of this method is a complex formation during titration. *Equipment*: Reagent 1 and reagent 2. Reagent 2 contains 3-aminopropyldimethylamine (*Riedel-de Haën AG*).

Total-Nitrogen

Equipment: HACH DR/2010, Nitrogen Total, Test'N Tube (0-25 mg/L N), TNT Persulfate Digestion Method. *Summary of Method:* An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after digestion to eliminate halide interference. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance at 410 nm. *Equipment;* HACH DR/2010 Spectrophotometer, Heating block, Total Nitrogen Hydroxide Reagent Vials, Total Nitrogen Persulfate Reagent Powder Pillows, TN Reagent B Powder Pillow, TN Reagent A Powder Pillow, TN Reagent C Vials. NH_3-N Standard Solution, 2mg/L and 10 mg/L (*HACH*

Company).

Nitrate

Equipment: HACH DR/700, Nitrate, LR (0-0.5 mg/L NO_3^-), Cadmium Reduction Method. *Summary of Method;* Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to chromatropic acid to produce a pink colored product. *Equipment;* HACH DR/700 Spectrophotometer, filter module 50.01, NitraVer 6, Nitrate Reagent Powder Pillow, NitriVer 3, Nitrite Reagent Powder Pillow, Nitrate Nitrogen Standard Solution, 0.1, 0.2, 0.3, 0.5 mg/L NO_3^-N. The NitraVer 6 Reagent contains cadmium. (*HACH Company, DR/700, 1997*). The waste water from the analysis that contains cadmium will be run through a filter. The cadmium waste is collected onto the filter. These filters will be brought back to Sweden for further waste disposal (*HACH Company)*.

Ammonia

Equipment: HACH DR/700, Nitrogen Ammonia (0-1.00 mg/L NH_3-N), Salicylate Method. *Summary of Method;* Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidised in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution. *Equipment;* HACH DR/700 Spectrophotometer, Filter module 61.01, Salicylate Reagent Powder Pillow, Alkaline Cyanurate Reagent Powder Pillow, 0.20 mg/L Ammonia Nitrogen Standard Solution (*HACH Company, DR/700).*

Total-Phosphorus

Equipment: HACH DR/2010, Phosphorus, Total (0.00-3.50 mg/L PO_4^{3-}), PhosVer 3 with Acid Persulfate Digestion *Summary of Method;* Orthophospahte reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. *Equipment;* HACH/2010 Spectrophotometer, heating block, 1.00 N sulphuric acid, Potassium Persulfate Powder Pillow, 1.00 N sodium hydroxide, PhosVer 3 Phosphate Reagent Powder Pillow, Phosphate Standard Solution 0.5 and 1.50 mg/L as $P0_4^{3-}$ (*HACH Company*).

Phosphate

Equipment: HACH DR/700, Phosphorus Reactive (0-2.50 mg/L PO_4^{3-}), PhosVer 3 (Ascorbic Acid) Method. *Summary of Method;* Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. *Equipment;* HACH DR/700 Spectrophotometer, Filter Module 81.01, PhosVer 3 Phosphate Reagent Powder Pillow, Phosphate Standard Solution 0.1, 0.2 mg/L as $P0_4^{3-}$ (*HACH Company).*

COD

Equipment: HACH DR/700, Oxygen Demand Chemical (COD), (0-150 mg/L). Reactor Digestion Method. *Summary of Method;* The mg/L COD results are defines as the mg of O_2consumed per litre of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidising agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{3+}$) to green chromic ion (Cr^{3+}). When the 0-150 mg/L colorimetric or titrimetric methods are used, the amount of Cr^{6+} is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences. *Equipment;* HACH DR/700, Filter module 42.01, heating block, COD Digestion Reagent Vials, COD Standard Solution 100 mg/L (*HACH Company, DR/700, 1997).* The waste water from the analysis that contains mercury ions will be run through a filter. The mercury waste is collected onto the filter. These filters will be brought back to Sweden for further waste disposal (*HACH Company).*